

Magnetic Frustration in a Mn Honeycomb Lattice Induced by Mn-O-O-Mn Pathways

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(Dated: January 17, 2011)

We investigated the electronic structure of layered Mn oxide $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ with a Mn honeycomb lattice by x-ray absorption spectroscopy. The valence of Mn was determined to be 4+ with a small charge-transfer energy. We estimated the values of superexchange interactions up to the fourth nearest neighbors (J_1 , J_2 , J_3 , and J_4) by unrestricted Hartree-Fock calculations and a perturbation method. We found that the absolute values of J_1 through J_4 are similar with positive (antiferromagnetic) J_1 and J_4 , and negative (ferromagnetic) J_2 and J_3 , due to Mn-O-O-Mn pathways activated by the smallness of charge-transfer energy. The negative J_3 provides magnetic frustration in the honeycomb lattice to prevent long-range ordering.

PACS numbers: 71.30.+h, 71.28.+d, 79.60.Dp, 73.61.-r

Since the resonating valence bond state in geometrically frustrated magnets has been proposed by Anderson [1], spin-disordered ground states in Mott insulators on frustrated lattices have been attracting great interest in condensed-matter physics. The exchange interaction J in a Mott insulator is roughly given by $-2t^2/E_g$, where t is the transfer integral between the two localized orbitals and E_g is the excitation energy across the Mott gap. In Mott insulators on frustrated lattices, spin-disordered systems including organic and inorganic materials [2–6] all have relatively small E_g , suggesting that the smallness of E_g or the closeness to the Mott transition would be important to realize the spin-disordered ground states.

Various insulating transition-metal oxides are known as Mott insulators and can be classified into (i) the Mott-Hubbard type insulators where the Mott gap E_g is mainly determined by the Coulomb interaction U between the transition-metal d electrons and (ii) the charge-transfer type insulators where E_g is determined by the charge-transfer energy Δ from the oxygen p state to the transition-metal d state [7]. Therefore, the smallness of E_g can be obtained in transition-metal oxides with small U or small Δ . In the small U case, theoretical studies on triangular-lattice Hubbard models proved that a spin-disordered phase is realized near the Mott transition [8–11], which could be related to the higher order exchange terms. As for the small Δ case, in addition to

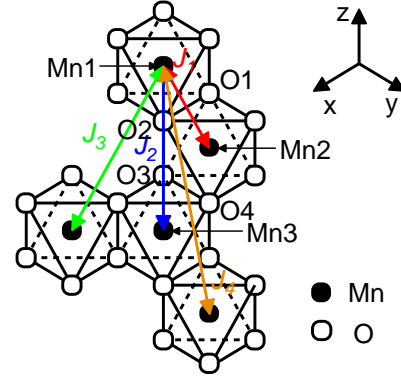


FIG. 1: (Color online): Network of MnO_6 octahedrons in the honeycomb lattice with the definitions of interactions in the nearest-neighbor J_1 , the second nearest-neighbor J_2 , the third nearest-neighbor J_3 , and the fourth nearest neighbor J_4 .

the higher order terms, the exchange pathways through the oxygen p state may give unexpectedly long ranged exchange terms and may affect the spin disordering.

Very recently, a spin-disordered ground state is reported in a layered Mn oxide $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ with a Mn honeycomb lattice in which the exchange interaction between second neighbor Mn sites introduces a kind of frustration in the honeycomb lattice [12]. In this material, there is a network of MnO_6 octahedrons and Fig. 1 shows the definitions of interactions in the nearest-neighbor J_1 , the second nearest-neighbor J_2 , the

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third nearest-neighbor J_3 , and the fourth nearest neighbor J_4 . The exchange interaction J_2 between second neighbor sites could be derived from the Mn-O-O-Mn exchange pathways which becomes important in small Δ systems. The values of these interactions were studied both theoretically [13] and experimentally by inelastic neutron scattering [14]. In these studies, only J_1 and J_2 are considered by assuming that the values of J_3 and J_4 are small enough to be neglected. However, since the exchange interaction J_3 between the third neighbor sites is also derived from the Mn-O-O-Mn exchange pathways, it is not a trivial question whether J_3 is negligible compared to J_2 or not. In this context, it is very interesting and important to study the electronic structure of the Mn oxide, especially the values of interactions J_1 - J_4 , using spectroscopic methods and to reveal the origin of the spin-disordered state from the electronic structural viewpoint. In this paper, we investigated the electronic structure of this material by x-ray absorption spectroscopy (XAS), and also estimated the values of magnetic interactions. Unrestricted Hartree-Fock calculations and a perturbation method revealed that the nearest neighbor and fourth nearest neighbor J_1 and J_4 are positive (antiferromagnetic), and the next nearest neighbor and third nearest neighbor J_2 and J_3 are negative (ferromagnetic). In the present analysis, the ferromagnetic J_2 does not introduce magnetic frustration in the honeycomb lattice. We conclude that the ferromagnetic J_3 is the origin of magnetic frustration and the absence of long-range ordering in this material.

The synthesis of $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ polycrystalline powder is described in Ref. [12]. X-ray absorption experiments were performed at 11ID-1 (SGM) of the Canadian Light Source. The spectra were measured in the total-electron-yield (TEY) mode. The total energy resolution was set to 100 meV. All the spectra were measured at room temperature. The obtained spectrum is analyzed by standard cluster-model calculations [15] to obtain electronic parameters. The parameters in this model are $3d$ - $3d$ and $3d$ - $2p$ Coulomb interactions (U_{dd} and U_{dc} , respectively), charge-transfer energy from O $2p$ to Mn $3d$ states Δ , hopping integrals between Mn $3d$ and O $2p$ molecular states [$V(t_{2g})$ and $V(e_g)$], and crystal field parameter $10Dq$. The superexchange interactions are evaluated using unrestricted Hartree-Fock calculation with a multi-band d - p Hamiltonian with Mn $3d$ and O $2p$ states [16]. The Hamiltonian is given by

$$H = H_p + H_d + H_{pd},$$

$$H_p = \sum_{k,l,\sigma} \epsilon_k^p p_{k,l\sigma}^+ p_{k,l\sigma} + \sum_{k,l>l',\sigma} V_{k,ll'}^{pp} p_{k,l\sigma}^+ p_{k,l'\sigma} + H.c.,$$

$$\begin{aligned} H_d = & \sum_{k,m\sigma} \epsilon_d d_{k,m\sigma}^+ d_{k,m\sigma} \\ & + \sum_{k,m>m',\sigma} V_{k,mm'}^{dd} d_{k,m\sigma}^+ d_{k,m'\sigma} + H.c. \\ & + u \sum_{i,m} d_{i,m\uparrow}^+ d_{i,m\uparrow} d_{i,m\downarrow}^+ d_{i,m\downarrow} \\ & + u' \sum_{i,m\neq m'} d_{i,m\uparrow}^+ d_{i,m\uparrow} d_{i,m'\downarrow}^+ d_{i,m'\downarrow} \\ & + (u' - j') \sum_{i,m>m',\sigma} d_{i,m\sigma}^+ d_{i,m\sigma} d_{i,m'\sigma}^+ d_{i,m'\sigma} \\ & + j' \sum_{i,m\neq m'} d_{i,m\uparrow}^+ d_{i,m\uparrow} d_{i,m\downarrow}^+ d_{i,m\downarrow} \\ & + j \sum_{i,m\neq m'} d_{i,m\uparrow}^+ d_{i,m\uparrow} d_{i,m'\downarrow}^+ d_{i,m'\downarrow}, \end{aligned}$$

$$H_{pd} = \sum_{k,m,l,\sigma} V_{k,lm}^{pd} d_{k,m\sigma}^+ p_{k,l\sigma} + H.c.$$

Here, $d_{i,m\sigma}^+$ are creation operators for the Mn $3d$ electrons at site i . $d_{k,m\sigma}^+$ and $p_{k,l\sigma}^+$ are creation operators for Bloch electrons with momentum k which are constructed from the m -th component of the Mn $3d$ orbitals and from the l -th component of the O $2p$ orbitals, respectively. The intra-atomic Coulomb interaction between the Mn $3d$ electrons is expressed using Kanamori parameters, u , u' , j and j' satisfying the relations $u = u' + j + j'$ and $j = j'$. The transfer integrals between the Mn $3d$ and O $2p$ orbitals $V_{k,lm}^{pd}$ are given in terms of Slater-Koster parameters ($pd\sigma$) and ($pd\pi$). The parameters determined by the cluster-model calculation are used as input of the unrestricted Hartree-Fock analysis.

Figure 2 shows the Mn $2p$ XAS spectrum of $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$. There are two structures, Mn $2p_{3/2} \rightarrow 3d$ absorption at 640 - 650 eV and Mn $2p_{1/2} \rightarrow 3d$ absorption at 650 - 660 eV. The experimental spectrum has a sharp peak at ~ 641.5 eV characteristic of Mn^{4+} , concluded by comparing with the reference data of Mn^{2+} (MnO), Mn^{3+} (LaMnO_3), and Mn^{4+} ($\text{EuCo}_{0.5}\text{Mn}_{0.5}\text{O}_3$ and SrMnO_3) from Ref. [17]. This indicates that the valence of Mn is $4+$ in $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$, consistent with the valence state of $\text{Bi}_3^{3+}\text{Mn}_4^{4+}\text{O}_{12}^{2-}(\text{NO}_3)^-$ obtained in Ref. [12]. We performed configuration-interaction (CI) cluster-model calculations [15] to obtain electronic parameters. Here we fixed the following values $U_{dd} = 6.0$ eV, $U_{dc} = 7.5$ eV, $V(e_g) = 3.0$ eV, and $10Dq = 1.3$ eV and changed the value of Δ from 0.0 eV to 4.0 eV, as shown in Fig. 2 (a). The calculated spectra do not depend on the value of Δ so much, but the small Δ values of 1.0 ± 1.0 eV reproduce the experiment most successfully from a peak at ~ 641.5 eV and Mn $2p_{1/2}$ structures.

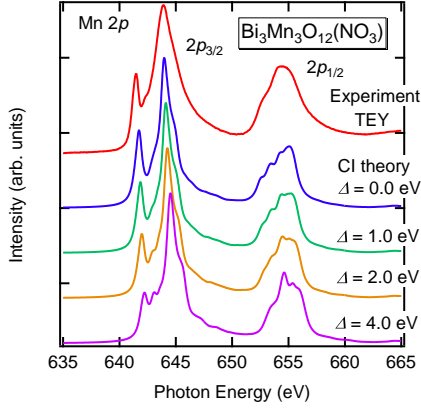


FIG. 2: (Color online): Mn 2p XAS spectra of $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ and comparison with the CI theory.

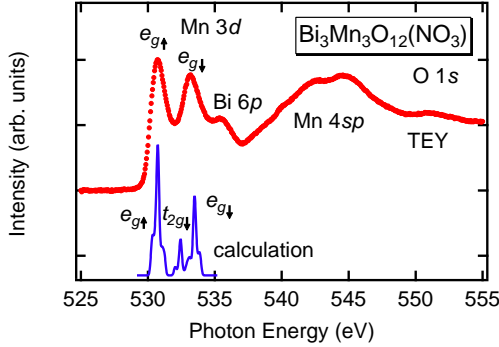


FIG. 3: (Color online): O 1s XAS spectra of $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ together with the calculated O 1s partial density of states by unrestricted Hartree-Fock calculations.

Figure 3 shows the O 1s XAS spectrum of $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ and the calculated O 1s partial density of states by unrestricted Hartree-Fock calculations. There are two structures in the O 2p - Mn 3d hybridized states, assigned as majority-spin e_g states ($e_{g\uparrow}$) and minority-spin e_g states ($e_{g\downarrow}$), and another structure in the O 2p - Bi 6p states as shown in Fig. 3. There is a higher intensity at $e_{g\downarrow}$ states in the experiment than in the calculation, indicating that there is a substantial Bi 6p contribution also in this structure. These assignments are consistent with the Mn^{4+} (d^3) state, where majority-spin t_{2g} states are occupied by electrons.

In order to obtain the values of magnetic interactions, we have performed unrestricted Hartree-Fock analysis on the multiband $d-p$ Hamiltonian with the Mn 3d and O 2p orbitals. Δ , U , and $(pd\sigma)$ were set to be 1.0, 6.0, and -1.8 eV, respectively, on the basis of the cluster model analysis. The ratio $(pd\sigma)/(pd\pi)$ is -2.16 . Remaining transfer integrals expressed by $(pp\sigma)$, $(pp\pi)$, $(dd\sigma)$, and $(dd\pi)$ are fixed at -0.6 , 0.15 , -0.3 , and 0.15 eV, respectively, for the honeycomb lattice with the regular MnO_6 octahedron. Here Δ denotes the charge-transfer energy

for Mn^{4+} specifically $\Delta = \epsilon_d - \epsilon_p + 3U$.

With this parameter set, the lowest energy state is found to be the conventional antiferromagnetic state where the first neighboring sites are antiferromagnetically coupled. In the antiferromagnetic ground state, the second, third, and fourth neighboring sites are ferromagnetically, antiferromagnetically, and antiferromagnetically coupled, respectively. We have calculated energies of ferromagnetic state as well as modified antiferromagnetic states which are obtained by exchanging spins of some neighboring sites in the ground state. As expected, the ferromagnetic state is very much higher in energy than the antiferromagnetic ground state. However, some of the modified antiferromagnetic states were found to have energies very close to that of the ground state. By mapping the Hartree-Fock energies to the Heisenberg model with J_1 , J_2 , J_3 , and J_4 , the obtained values are:

$$\begin{aligned} J_1 &= 9.15 \text{ meV} \\ J_2 &= -5.32 \text{ meV} \\ J_3 &= -4.80 \text{ meV} \\ J_4 &= 5.77 \text{ meV} \end{aligned} \quad (1)$$

While the antiferromagnetic J_1 and ferromagnetic J_2 , and antiferromagnetic J_4 are consistent with the antiferromagnetic ground state, the ferromagnetic J_3 can introduce frustration effect on it. Since the magnitude of the ferromagnetic J_3 is comparable to those of the antiferromagnetic J_1 and ferromagnetic J_2 , the ferromagnetic J_3 by the Mn-O-O-Mn superexchange pathways is responsible for the absence of long-range ordering in the present honeycomb system.

Let us also examine the sign of J_3 by considering superexchange pathways in $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ using a perturbation method based on the electronic structure parameters obtained from the analysis of the Mn 2p XAS spectrum. Here, we will use Slater-Koster parameters, $(pp\sigma)$, $(pd\sigma)$, $(dd\sigma)$, and so on [18].

J_3 is given as

$$\begin{aligned}
J_3 = & \left(\frac{(pd\pi)^4}{[\Delta - (pp\sigma)/2 + (pp\pi)/2]^2} + \frac{(pd\pi)^4}{[\Delta + (pp\sigma)/2 - (pp\pi)/2]^2} \right) \left(\frac{1}{\Delta + u_p} + \frac{1}{u} \right) \\
& + \frac{2(pd\pi)^4}{2(pd\pi)^4} \times \left(\frac{1}{\Delta + u_p} + \frac{1}{u} - \frac{1}{\Delta + u_p - j_p} \right) \\
& - \left(\frac{(pd\sigma)^2(pd\pi)^2}{[\Delta - (pp\sigma)/2 - (pp\pi)/2]^2} + \frac{(pd\sigma)^2(pd\pi)^2}{[\Delta + (pp\sigma)/2 + (pp\pi)/2]^2} \right) \times \\
& \left(\frac{1}{\Delta + u_p} + \frac{1}{u - 3j} - \frac{1}{u - 2j} \right) \\
& - \frac{2(pd\sigma)^2(pd\pi)^2}{2(pd\sigma)^2(pd\pi)^2} \times \left(\frac{1}{\Delta + u_p} + \frac{1}{u - 3j} - \frac{1}{\Delta + u_p - j_p} - \frac{1}{u - 2j} \right) \\
\sim & \frac{2(pd\pi)^4}{\Delta^2} \left(1 - \frac{[(pp\sigma)/2 - (pp\pi)/2]^2}{\Delta^2} \right) \frac{1}{\Delta + u_p} \\
& + \frac{4(pd\pi)^4[(pp\sigma)/2 - (pp\pi)/2]^2}{\Delta^4} \left(\frac{1}{u} - \frac{j_p}{(\Delta + u_p)^2} \right) \\
& - \frac{2(pd\sigma)^2(pd\pi)^2}{\Delta^2} \left(1 - \frac{[(pp\sigma)/2 + (pp\pi)/2]^2}{\Delta^2} \right) \frac{1}{\Delta + u_p} \\
& - \frac{4(pd\sigma)^2(pd\pi)^2[(pp\sigma)/2 + (pp\pi)/2]^2}{\Delta^2} \times \left(\frac{j}{u^2} - \frac{j_p}{(\Delta + u_p)^2} \right)
\end{aligned} \tag{2}$$

Here we considered the molecular orbitals made from two oxygen sites. The first and second terms proportional to $(pd\pi)^4$ are given by the pathway from the Mn t_{2g} states to the O $2p$ molecular orbitals to the Mn t_{2g} states. The third and fourth terms proportional to $(pd\sigma)^2(pd\pi)^2$ are given by the pathway from the Mn e_g states to the O $2p$ molecular orbitals to the Mn t_{2g} states. J_3 is dominated by the negative third term and causes ferromagnetic interactions, which is consistent with the result of the unrestricted Hartree Fock calculations.

From the neutron measurements, it was found that the values of interlayer interactions (J_c) are also comparable to J_1 [14]. This is consistent with our result because J_c is also determined by Mn-O-O-Mn pathways.

We investigated the electronic structure of $\text{Bi}_3\text{Mn}_4\text{O}_{12}(\text{NO}_3)$ by XAS. The valence of Mn was determined to be 4+, and from CI theory we found that a charge-transfer energy is small in this material. Then we estimated the values of $J_{1,2,3,4}$ by unrestricted Hartree-Fock calculations and a perturbation method. We found antiferromagnetic J_1 and ferromagnetic J_2 and J_3 , leading to the existence of magnetic frustration and the absence of long-range ordering, as experimentally confirmed.

The authors would like to thank Y. Motome for informative discussions. This research was made possible with financial support from the Canadian funding organizations NSERC, CFI, and CIFAR. H.W. is supported by the Japan Society for the Promotion of Science (JSPS) through its Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program).

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